

MICROSCOPIC EVIDENCE OF COMPETING HYDROGENATION AND
CONDENSATION REACTIONS DURING COAL LIQUEFACTION

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INTRODUCTION

Reflectance characteristics of vitrinite-derived residues from coal liquefaction provide a measure of the response of coals to reaction conditions (1-3). The presence of a low-reflecting primary vitroplast (4,5), an isotropic pitch-like material formed by simple melting of vitrinite, indicates that depolymerization reactions were incomplete. Low-reflecting secondary vitroplast (5), formed by precipitation from the solubilized products, suggests that the coal had been at least partially hydrogenated. High-reflecting vitroplast or vitrinite residue indicates that condensation reactions had predominated. The presence together of the last two of these residue types indicates that hydrogenation and condensation have been locally competing reactions following thermolysis.

This paper discusses the use of residue microscopy in evaluating the influence of a dispersed molybdenum catalyst, of reactor atmosphere, of a pretreatment stage and of coal rank in bench-scale liquefaction experiments.

EXPERIMENTAL

The four coals used in this study (lig, subB, hvC and hvA bituminous) were obtained from the Penn State Coal Sample Bank. Some of their relevant properties are listed in Table I.

Hydrogenation reactions were performed, mostly without a solvent vehicle (i.e., dry), in batch stainless-steel tube reactors (approx. 25 cm³ capacity) (6, 7). Approximately 5 g of coal (-60 mesh U.S. sieve size) were charged to the reactor for the dry runs. For hydrogenations conducted with added solvent, 2.5 g of coal and 5 g of solvent were used. If catalyst was present (as 1% sulfided Mo on dmmf coal), a stoichiometric amount of CS₂ was added to ensure that enough available sulfur was present to convert the metal to its sulfide form. The assumption was made that ammonium tetrathiomolybdate (ATM) would convert entirely to MoS₂. The procedure employed for preparing the ATM and dispersing it on the coal, and reference to the metastability of this catalyst precursor are described elsewhere (8, 9).

The loaded reactor was purged of air with nitrogen and then purged three times with the desired gas (hydrogen or nitrogen) before finally being pressurized

to 7 MPa cold pressure. The reactor contents were agitated vertically through 2.5 cm at about 200 cycles per minute by an electrically driven cam system while the reactor was immersed in a preheated, fluidized sandbath. After reaction for the desired time, the reactor was removed from the sandbath and quenched to room temperature by immersion in cold water. First-stage reactions were conducted at 275°C, and the second stage at 425°C, both for 30 min.

In between the steps of the temperature-staged liquefaction experiments, the reactor was quenched and the gaseous products vented. The reactor was then repressurized with 7 MPa hydrogen and reaction was continued at the higher temperature. This procedure was adopted to circumvent the possibility of limiting the hydrogen partial pressure.

Liquefaction experiments were done in duplicate. The products of one of the reactors were used for microscopy. The second reactor was vented and the remaining liquefaction products washed out and extracted with tetrahydrofuran (THF) to determine percent conversion.

RESULTS AND DISCUSSION

Non-Catalytic Reactions

Preceding a coal liquefaction reaction with a low-temperature pretreatment stage has been shown to have a profound effect on conversion and product selectivity, particularly where catalysts are employed in the reaction (1). Consequently, some detailed microscopy was performed on residues that represent pretreatment conditions alone. Three of the coals which had been reacted at 275°C (PSOC-1482, 1401 and 1504) under different atmospheres were evaluated to determine whether there had been any discernible changes in the structure of the reacted coal.

Following pretreatment (first stage) conditions the lignite and subbituminous coals showed almost no microscopic evidence of change in the coal structure other than some separation of coal particles along bedding planes. It is important to note that the vitrinite/huminite macerals showed no rims of low reflectance that would signify that hydrogenation has proceeded via a shell progressive mechanism. Also, there was no evidence of maceral devolatilization or the onset of fluidity that would help to explain the improved conversion and product selectivity that occurs when a low-temperature pretreatment is employed prior to reaction under full liquefaction conditions. Maximum reflectance values were measured for a selection of residues from pretreated coals and are presented in Figure 1. Compared to the reflectance of the feed coal, little change was observed following pretreatment. Only in the case of the subbituminous coal was there a significant increase. These general relationships are consistent whether a hydrogen or a nitrogen atmosphere was employed during the reaction (Table 2).

The same similarity between reflectances of residues from runs in nitrogen and hydrogen was found for the higher temperature and temperature-staged experiments (Table 2). This is somewhat surprising given the fact that the best conversion was observed for the temperature-staged reaction of the bituminous coal in a hydrogen environment. These observations suggest that the reflectance

increase of vitrinite-derived residual material from runs made in the absence of a solvent may be more related to the maximum temperature employed in the reaction than to the reactant gas.

Major changes in the appearance and optical properties of residues were observed following the high-temperature (425°C) and temperature-staged reactions. For the most part the liptinite macerals had been converted and were no longer present in the residues. Huminite/vitrinite remnants and vitroplast were the predominant components found in residues of the lignite (PSOC-1482) and subbituminous (PSOC-1401) coals, whereas vitroplast was the dominant component found in residues from the hvCb (PSOC-1498) and hvAb (PSOC-1504) coals. The maximum reflectances of these residue components were greatly increased over those of the original coal. Fig. 1 compares the trends in reflectance for the different hydrogenation conditions and coals used during this project. For lower coal ranks, temperature-staged residues have a higher reflectance than the single-stage high-temperature liquefaction residues. Reflectance is lower for temperature-staged compared to high-temperature reactions for the hvC and A bituminous coals. If higher reflectance is indicative of a greater degree of molecular condensation, then these data suggest that the lower rank coals have a greater tendency to condense under temperature-staged, dry, non-catalytic liquefaction than the conventional high-temperature liquefaction. The reversal of this tendency, and therefore a lower degree of molecular condensation under temperature-staged conditions, is seen in the residues from the higher rank coals. Finally, the reflectance values measured for both the temperature-staged and high-temperature residues of PSOC-1498 are somewhat low compared to the other coals (Fig. 1). We suspect that the maximum temperature (425°C) used for liquefaction of this hvCb coal may be too low to be optimal. Conversion yield for this coal (PSOC-1498) also supports this conclusion, averaging 21% compared to 34% conversion for the other coals.

Analysis of Extracted Residues to Determine Effects of Molybdenum Sulfide Catalyst

The general relationship in the reflectance of vitrinite-derived residues between non-catalytic and catalytic (1% Mo) temperature-staged hydrogenation experiments is provided in Fig. 2. This figure shows that the residual materials from the catalytic runs generally have higher reflectances than those from non-catalytic runs. The higher volumetric conversion of each coal in the presence of the molybdenum catalyst means that there is much less of the original coal material remaining; therefore, the residues will be of higher molecular weight and more highly condensed than from runs which achieve significantly lower levels of conversion. Another possible contribution to the higher reflectances would result from the catalyst promoting dehydrogenation reactions.

The significance of the foregoing is that a reflectance measurement made on residual material, considered in isolation from all pertinent information, may not be a good indication of the conversion of coal to a soluble product. In particular, low molecular weight products generated as a result of efficient hydrogenation are presumed to have had a relatively low reflectance; however, these materials will have dissolved in the solvent (THF) used to separate the soluble products from the insoluble residues. Because of this problem, a series of experiments was undertaken specifically to study the reflectance distribution

of the whole products (without extraction), as well as the insoluble residues of catalytic and non-catalytic temperature-staged hydrogenation. The results, are summarized in the section entitled "Analyses of Whole Products".

Reflectance analyses also were performed on just the THF-insoluble residues of dry catalytic and non-catalytic, single- and two-staged liquefaction of the subbituminous coal (PSOC-1401) reacted under N_2 and H_2 atmospheres and a combination of the two gases. This series of runs has enabled the influence of atmosphere, catalyst and pretreatment to be evaluated. Table 3 shows that, for both catalytic and non-catalytic runs, vitrinite reflectance values of the residues of pretreatment are low whether generated in a nitrogen or a hydrogen atmosphere. The influence of atmosphere and catalyst becomes more evident as a result of high-temperature and temperature-staged reactions ($425^\circ C$). The vitrinite was subject to significant changes as shown by a large increase in maximum reflectance and by the qualitative descriptions provided in Table 3. In this table, "reacted" vitrinite (or vitroplast) refers to those vitrinite particles which had undergone thermoplastic deformation and might have developed a granular anisotropy; "unreacted" vitrinite refers to those showing no evidence of thermoplasticity, for the most part retaining their original morphology.

In the presence of the molybdenum catalyst and hydrogen atmosphere, most of the vitrinite particles became plastic in the reactor and were partially subject to condensation leading to the development of a granular anisotropy. In comparison, the other three high-temperature residues processed in a nitrogen atmosphere are composed mainly of "unreacted" vitrinite particles. This demonstrates that the presence of a catalyst and hydrogen gas play an important role in promoting vitrinite reactivity during liquefaction of the subbituminous coal. Although the "unreacted" vitrinite particles may possess a lower reflectance than the "reacted" particles, the latter were associated with a higher volumetric conversion.

During the temperature-staged reactions ($275^\circ C + 425^\circ C$), the effect of the first stage is negligible when a nitrogen atmosphere was used during the second stage. It was found, for residues of reactions at $425^\circ C$, N_2 ; $275^\circ C$, $N_2 + 425^\circ C$, N_2 ; and $275^\circ C$, $H_2 + 425^\circ C$, N_2 , that the reflectance values were very similar for residues of the catalytic runs and again for those from the non-catalytic runs (Table 3). This suggests that first-stage reactions did not play an important role in liquefaction if an inert atmosphere was used in the second stage. This is further supported by the conversion data for these groups of three reactions (Table 3).

The impact of first-stage reaction became important when a hydrogen atmosphere was employed. In all residues after two-stage reactions with a hydrogen atmosphere, no granular anisotropic carbons were formed from the subbituminous coal (PSOC-1401), whereas this material is present in the residue of the corresponding single, high-temperature stage reaction. Also, the reflectance of the "reacted" vitrinite only is lowest when a hydrogen atmosphere was used in both stages with the catalyst, representing the conditions which gave rise to the highest conversion. This implies that first-stage reaction may have created products or molecular structures which are not as likely to undergo the condensation reactions that would otherwise take place during the second stage.

During the temperature-staged reactions, the presence of the catalyst minimized retrogressive reactions in the subbituminous coal. The reflectance values of the residues from the non-catalytic runs are consistently higher than those of the catalytic ones in the temperature-staged reactions even though there may have been considerably lower conversion (Table 3).

In brief, the influence of different parameters on dry liquefaction are interrelated. The effects of atmosphere and catalysis are manifested during the second stage, whereas they have relatively little apparent effect during the first stage. The presence of a hydrogen gas and catalyst promotes the thermoplastic development of vitrinite in the tubing bomb reactor, in turn favoring liquid conversion as a consequence of enhanced hydrogen transfer and catalyst dispersion.

Analyses of Whole Products, Catalytic and Non-Catalytic

The advantage of performing reflectance analysis upon the whole products of reaction is that a better opportunity is provided for evaluating the efficiency of hydrogenation. As noted above, some of the products of hydrogenation which would be dissolved by the extraction solvent are available for study in addition to undissolved coal and any products of retrogressive condensation reactions. This type of analyses is possible only with the products of dry hydrogenation; when a vehicle solvent is used, the products have a tarry consistency and cannot be formed into a pellet or polished without prior extraction. Published work (2) on the experimental hydrogenation of an hvA bituminous coal has shown that thermal reactions produced only higher reflecting vitrinite-derived materials, but where a dispersed catalyst was employed the reflectance distribution was extended downwards to significantly lower levels. The lower reflecting population, in the latter case, was THF soluble and highly fluorescing under blue-light irradiation. This contrasted with the THF-insoluble and non-fluorescent nature of the higher reflecting population. It was concluded that the low-reflecting material generated under catalytic hydrogenation in these experiments probably was asphaltenic in nature.

Subsequent work (3) showed that although similar reflectance distributions were obtained for the vitrinite-derived materials in the whole products from the hydrogenation of hvA and C bituminous coals, the anisotropic textures of these materials were quite different. A fine-grained anisotropy was apparent in the product of the first of these coals, possibly because of the large size of molecules generated during catalytic liquefaction (the residue of the corresponding thermal run was isotropic). It is supposed that locally, in the absence of hydrogen, the molecular fragments would align and stack to give an anisotropic texture. The same coal catalytically hydrogenated in the presence of a distillate process solvent fraction (220-500°C-boiling H-coal fractionator bottoms from Consolidation Coal Company) produced only negligible anisotropic semicoke; apparently the solvent must aid the dispersal of free radicals so that there is a greater likelihood of hydrogenation. In the case of the hvC bituminous coal, no anisotropic semicoke was produced during the dry hydrogenation under either thermal or catalytic conditions. It was concluded that the aromatic fragments formed during catalytic hydroprocessing of this coal must be less planar than those from the hvA bituminous coal. The reported difference in conversion levels between coals of hvC and A bituminous rank (Figs 1 & 2), and the optical

textures of their respective residues appear to be manifestations of known differences in molecular structure between coals of these ranks. These results, then, illustrate how geochemistry affects coal structure, and the significant effect this can have upon reaction chemistry.

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Table 1. Coal Properties

Penn State Sample Number	PSOC-1482	PSOC-1401	PSOC-1498	PSOC-1504
Seam	Hager	Lower Wyodak	Madge	Upper Sunnyside
State	North Dakota	Wyoming	Colorado	Utah
ASTM Rank	11g	subB	hVc	hVA
Mean-Maximum Reflectance of Vitrinite (R _{max} , %)	0.39	0.42	0.60	0.80
Ultimate Analysis (% daf)				
Carbon	72.3	74.3	77.5	82.0
Hydrogen	2.3	5.2	5.5	5.8
Oxygen (by difference)	23.5+	19.3	14.7+	9.7+
Nitrogen	1.0	1.1	1.8	1.8
Organic Sulfur	0.9	0.2	0.6	0.8
Proximate Analysis (a.r.%)				
Moisture	34.7	16.3	9.5	3.4
Volatile Matter	28.1	37.7	38.0	37.5
Fixed Carbon	31.4	41.1	46.1	51.8
Ash	5.9	6.6	6.4	7.3
Petrographic Composition (vol %, mineral-free)				
Vitrinite	88	85	89	87
Liptinite	2	2	2	3
Inertinite	10	13	9	10
Chloroform-soluble extract (% dmmf)	1.76	NA	1.31	1.06

Table 2. Maximum Reflectance Measurements on Vitrinite-Derived THF-Insoluble Residue Material From Dry, Non-catalytic Liquefaction

Raw	275°C, H ₂	275°C, N ₂	425°C, H ₂	425°C, N ₂	275°C, H ₂ + 425°C, H ₂	275°C, N ₂ + 425°C, N ₂
PSOC-1482	0.39	0.39	0.38	1.40	1.42	1.43
PSOC-1401	0.42	0.57	0.56	1.25	1.41	1.40
PSOC-1504	0.80	0.76	0.73	1.38	1.36	1.35

Table 3. Maximum Reflectance of Vitrinite-Derived Residue Material (THF insolubles) from Liquefaction of PSOC-1401

Sample Identification	Dry, catalytic (1% MoS ₂)			Dry, non-catalytic		
	Reflectance, %	Vitrinite Type	Conversion, %	Reflectance, %	Vitrinite Type	Conversion, %
Raw	0.42	(unreacted)	—	0.42	(unreacted)	—
275°C, N ₂	0.62	(unreacted)	4.5	0.56	(unreacted)	7.7
275°C, H ₂	0.60	(unreacted)	4.1	0.57	(unreacted)	9.0
425°C, N ₂	1.25	(unreacted)	25.9	1.41	(unreacted)	32.0
425°C, H ₂	1.58	(reacted)	60.3	1.25	(unreacted)	33.7
275°C, N ₂ + 425°C, H ₂	1.46	(reacted)	58.7	1.62	(reacted)	41.0
275°C, H ₂ + 425°C, N ₂	1.24	(unreacted)	25.7	1.43	(unreacted)	32.0
275°C, N ₂ + 425°C, N ₂	1.19	(unreacted)	24.8	1.40	(unreacted)	32.2
275°C, H ₂ + 425°C, H ₂	1.40	(reacted)	67.4	1.41	(reacted)	40.4

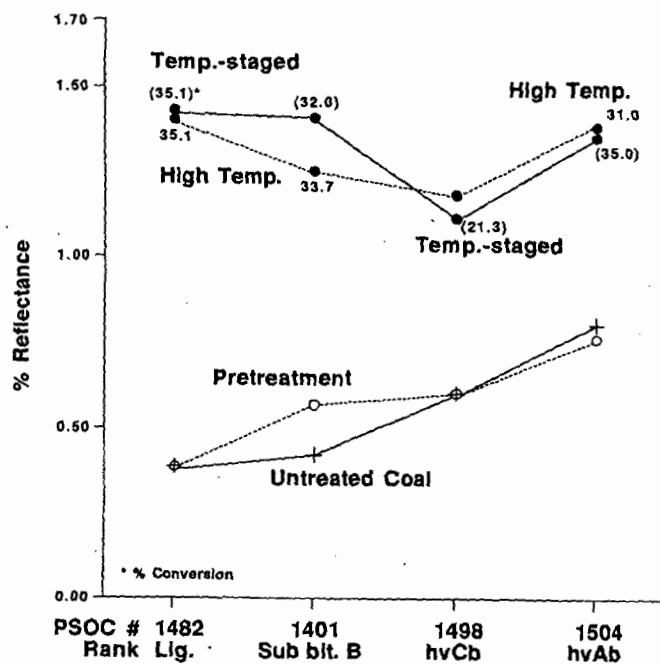


Figure 1. Mean Reflectance of Vitrinite-Derived Materials as a Function of Reaction Conditions; Dry, Non-catalytic Hydrogenation Residues

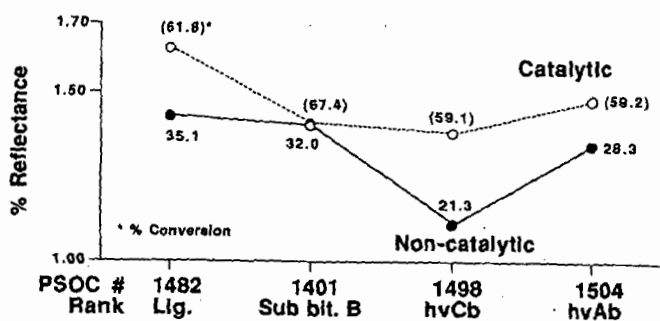


Figure 2. Mean Reflectance of Vitrinite-Derived Materials; Temp.-staged Dry, Catalytic (Mo) and Non-catalytic Hydrogenation Residues